Performance Effects of Electrode Processing for High-Energy Lithium-Ion Batteries

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ES313

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Overview

Timeline

- Task Start: 10/1/16
- Task End: 9/30/19
- Percent Complete: 20%

Barriers

- Barriers addressed
  - By 2022, further reduce EV battery cost to <$125/kWh.
  - Processing-property-performance knowledge gap.
  - Achieve deep discharge cycling target of 1000 cycles for EVs (2022).

Budget

- Total task funding
  - $1015k
- $315k in FY17

Partners

- Interactions/Collaborations
  - XALT Energy, Navitas Systems
  - ANL, Texas A&M
  - Ashland, JSR Micro, Solvay Specialty Polymers, Molecular Rebar Design
  - Frontier Industrial Technology, B&W MEGTEC
- Project Lead: ORNL

Relevance & Objectives

Main Objective: Generate deep understanding of process-property-performance relationships that lead to lower cost and higher performing lithium-ion cells.

- Optimize electrode formulation chemistry and dispersion mixing.
- Determine compatibility of Ni-rich cathodes (NMC and NCA) with water-based processing.
- Develop understanding of relationship between coating deposition physics, electrode quality, and electrode performance.
- Optimize drying and calendering protocols for thick electrodes.
- Reduce cell formation and electrode wetting time and elucidate impact on SEI and CEI layer chemistry, morphology, and functionality.
- Develop materials and chemical characterization methods for next-generation, high-speed electrode processing methods.

- **Relevance to Barriers and Targets**
  - Achieve ≥350 Wh/kg and ≥700 W/kg cell energy and power densities.
  - By 2022, reduce cell cost to $100-125/kWh.
  - 1000 deep discharge cycles with 80-90% capacity retention.

Task Milestones

Status	Milestones	Description
4/2017	FY17 Quarterly Progress Measure (12/2016)	Measure cathode active material stability as a function of exposure time in water (as a function of pH) and electrolyte for at least 5 cathode powders via ICP-MS; determine maximum exposure times for different cathode powders.
On Schedule	FY17 Milestone (9/2017)	Optimize Ni-rich NMC 622 or 811 aqueous dispersion formulation(s) for binder and dispersant molecular weight and concentration (with independent carbon black and active material formulations); obtain rate capability data and quantify capacity fade through at least 500 USABC 0.33C/-0.33C cycles while demonstrating an initial cell energy density rating of 225-250 Wh/kg (with upper cutoff voltage of 4.4 V or higher).

Approach

- **Problems to be addressed:**
  - *Ultimate cell cost and performance targets cannot be met without addressing the manufacturing science component of lithium-ion cells.*
  - Improper control or poor understanding of processing variables can dramatically affect cell performance.
  - Possible limitations of aqueous cathode processing may exist with Ni-rich cathodes and Si-based anodes.
  - Thick electrodes have many challenges, but they may be realized by thorough understanding of electrode processing variables.
- **Overall technical approach and strategy:**
  1. Enable thick electrode coatings with next generation cell chemistries (NMC 811, NCA, Si/graphite, etc.) through thorough understanding of colloidal science and formulation chemistry.
  2. In-depth study of interrelationship of electrode processing steps.
  3. Generate processing science knowledge that can be used to strengthen US domestic lithium-ion battery supply chain.
  4. Develop cohesive processing-property-performance database.
  5. Develop and utilize novel materials and chemical characterization techniques to shed light on active and inactive materials processibility.

Technical Accomplishments – Water and Electrolyte Stability Studies with Various NMC Materials

1) Expose 4 Different NMC Powders (NMC 333, NMC 532, NMC 622, NMC 811) to the following conditions for 3 different time periods (4 hours, 1 day, 1 week):
   - **Conditions:**
     1) Different pH values in water (Phase 1)
     2) Electrolyte after water exposure (Phase 2)
     3) Different electrolyte concentrations (Phase 3)
   - ***Meant to simulate processing conditions***
2) Analyze metal leaching in solutions by ICP-MS

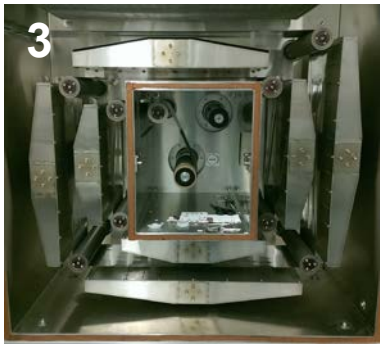
Phase 1: In Water	Phase 2: In Electrolyte After Water Exposure	Phase 3: In Electrolyte
pH 2	1.2 M $LiPF_6$ in 3:7 wt% EC/EMC After pH 2	0.6 M $LiPF_6$ in 3:7 wt% EC/EMC
pH 6.6 (DI Water)	1.2 M $LiPF_6$ in 3:7 wt% EC/EMC After pH 6.6	1.2 M $LiPF_6$ in 3:7 wt% EC/EMC
pH 12	1.2 M $LiPF_6$ in 3:7 wt% EC/EMC After pH 12	2.4 M $LiPF_6$ in 3:7 wt% EC/EMC

Experimental Design For Simulating Electrode Processing

Electrode Processing

Slurry Preparation

Electrode Coating



Electrode Drying

Secondary Drying

Pouch Cell Assembly

Stability Study

NMC Powder Exposed to Water for Different Time Periods

Filter

Solution Analyzed by ICP-MS ***Phase 1***

Powder Dried in Oven

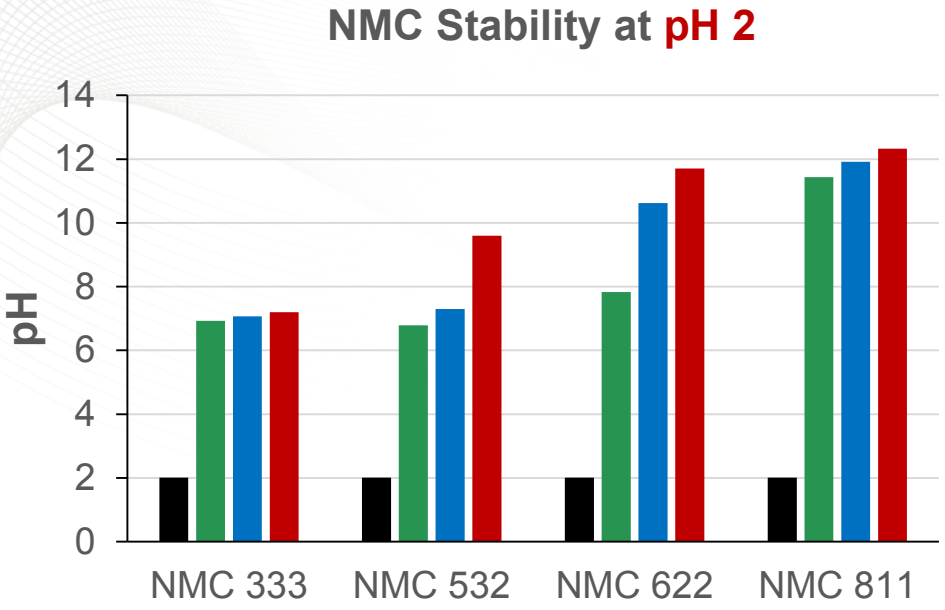
Powder Exposed to Electrolyte

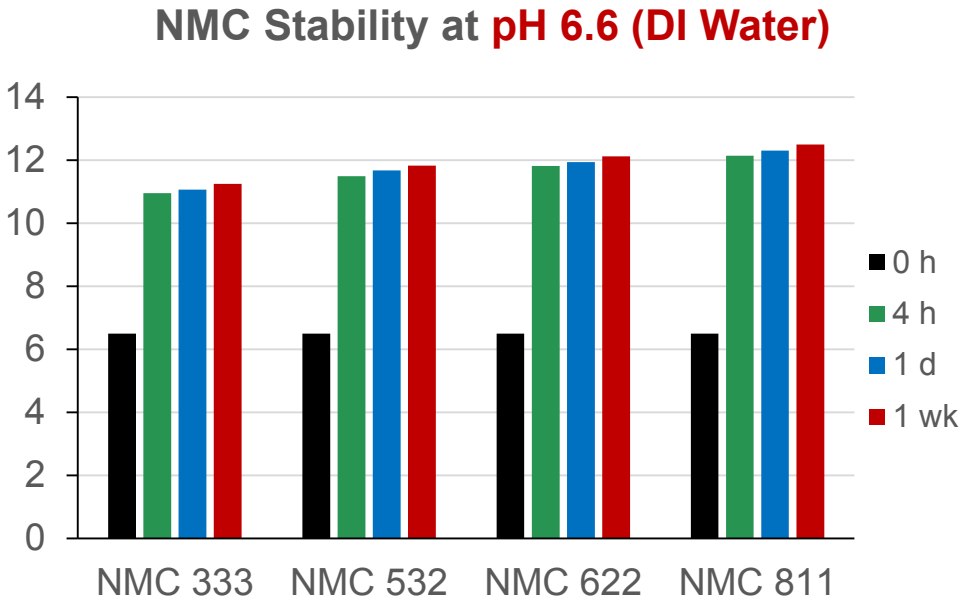
Filter

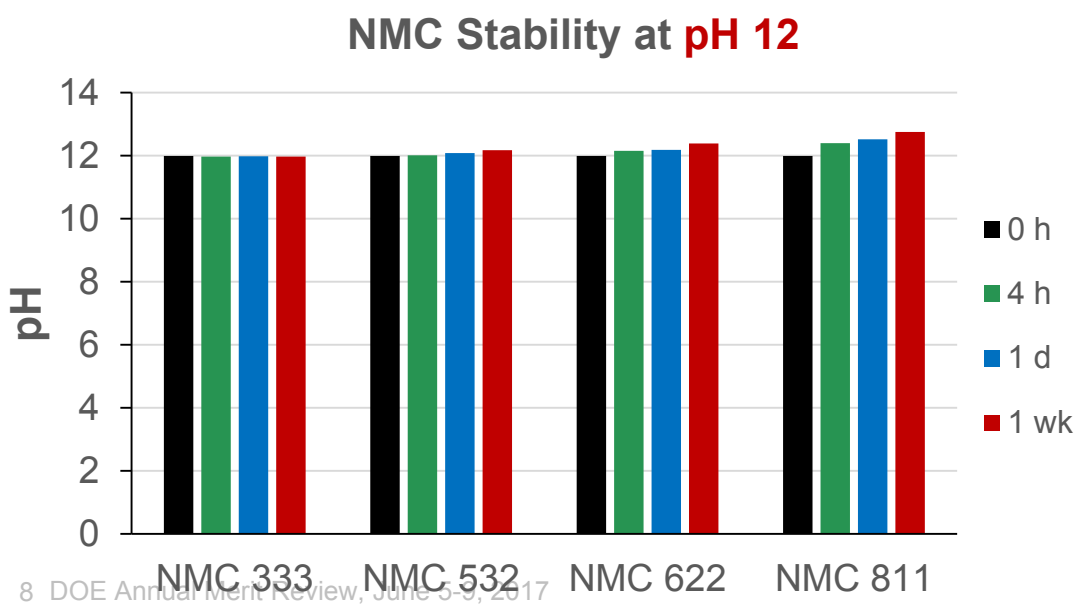
Solution Analyzed by ICP-MS ***Phase 2***

Worst case scenario*: much higher ratio of water to powder than we actually use*

NMC Stability Studies: pH Measurements





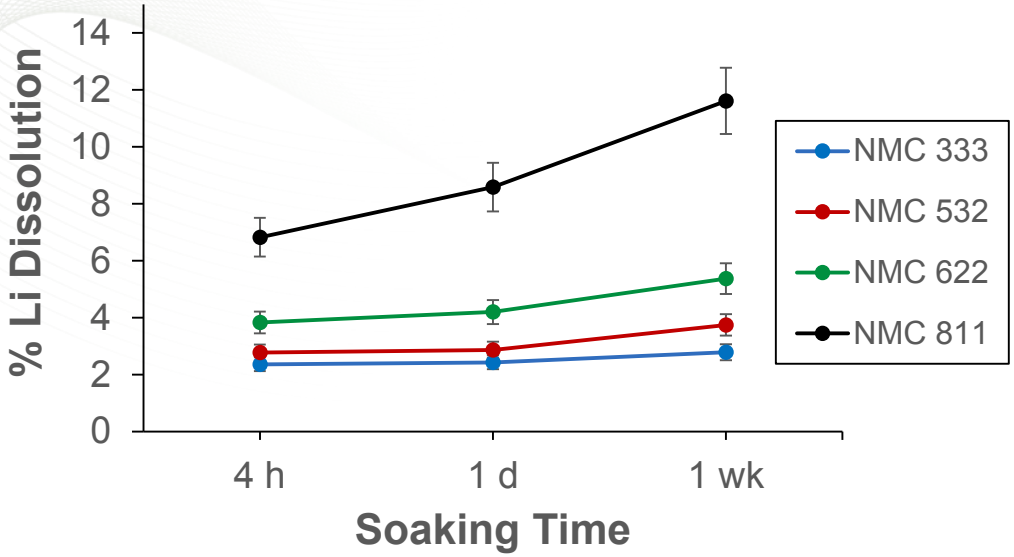


Conclusions:

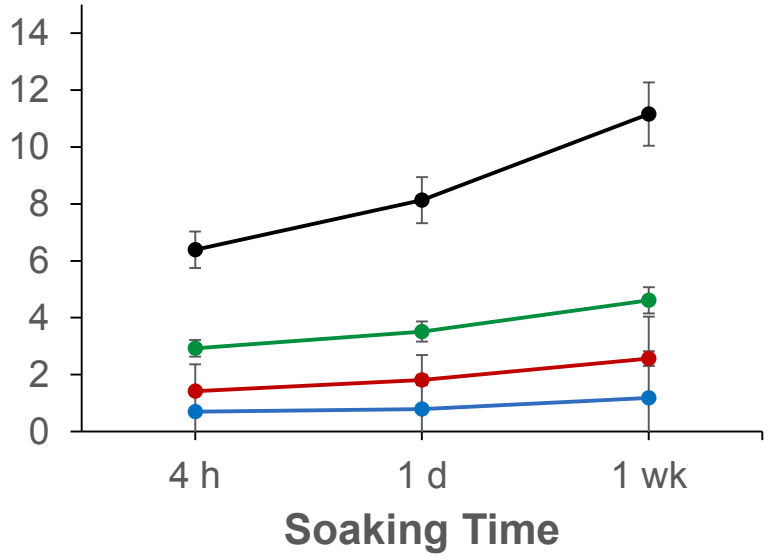
1) Almost all of the samples became basic after NMC soaking.
2) The longer the NMC was allowed to soak, the higher the resulting pH.
3) Samples at pH 2 are the least stable, while those at pH 12 are the most stable.
4) The higher the nickel content in the NMC, the higher the resulting pH (NMC 811 is the least stable).

ICP-MS Results: Li Leaching May Be Problematic

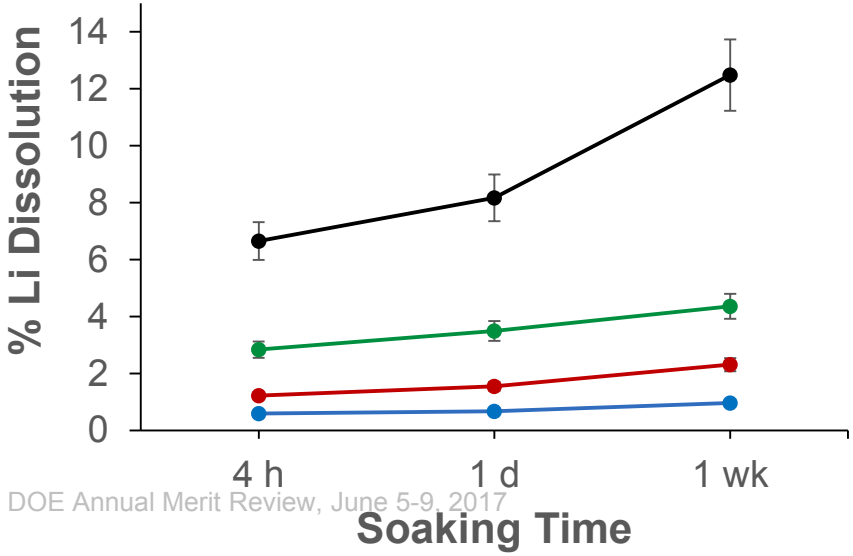
Li Leaching at **pH 2**



Li Leaching at **pH 6.6 (DI Water)**



Li Leaching at **pH 12**



Conclusions:

- Li leaching:
  1) Increases with increasing Ni content (NMC 811 has the highest leaching)
  2) Increases with longer soaking time
  3) Is generally slightly higher at pH 2

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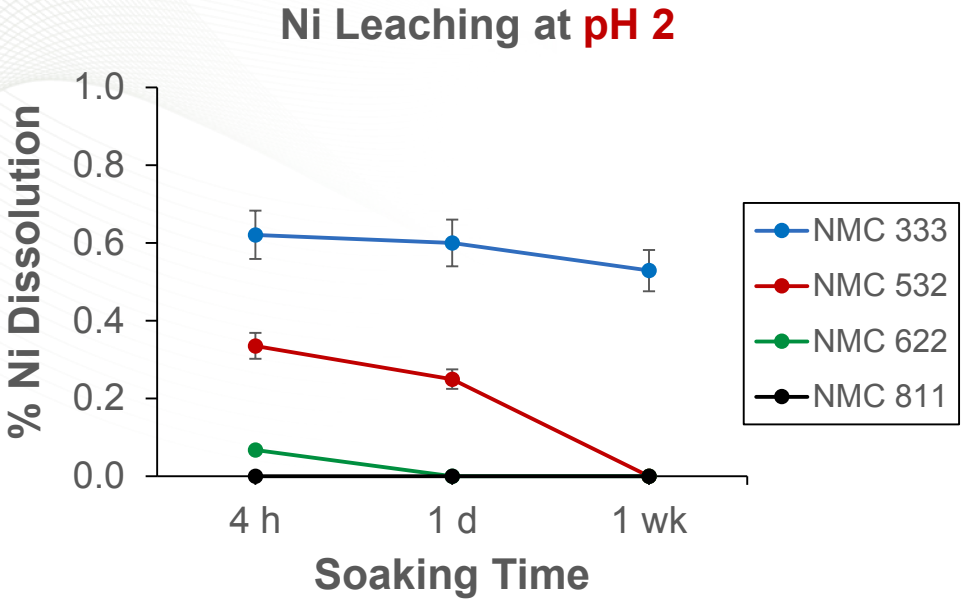
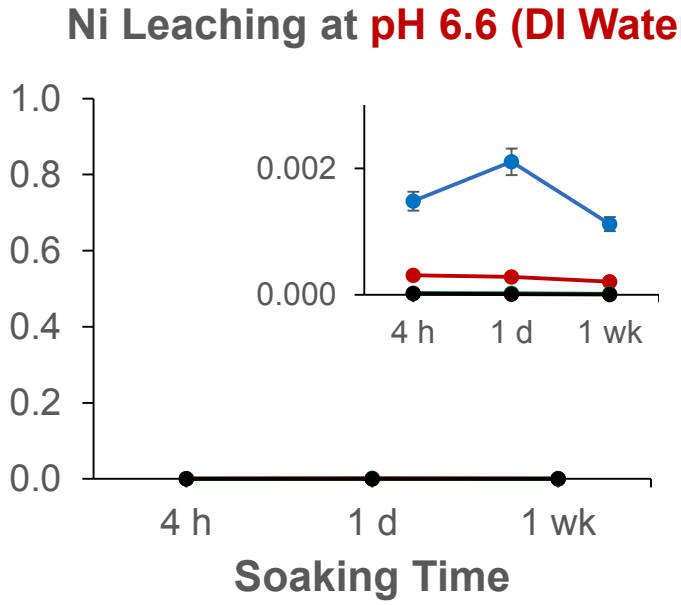
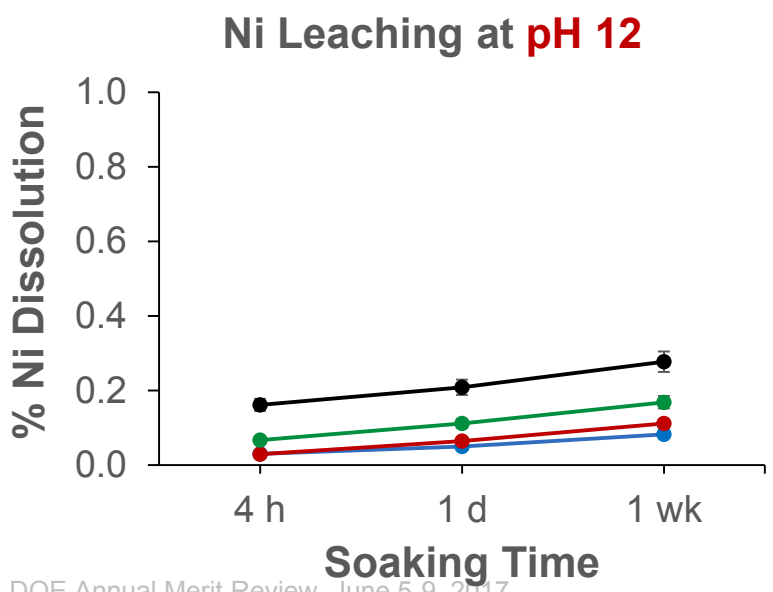
ICP-MS Results: Ni Leaching







Conclusions:

1) Higher Ni leaching at pH 2
2) Ni leaching shows opposite trends at high and low pH
   - Decreases with soaking time at pH 2 (may be a reprecipitation process and needs further investigation)
   - Increases with soaking time at pH 12
3) Negligible Ni leaching in DI water (pH 6.6)

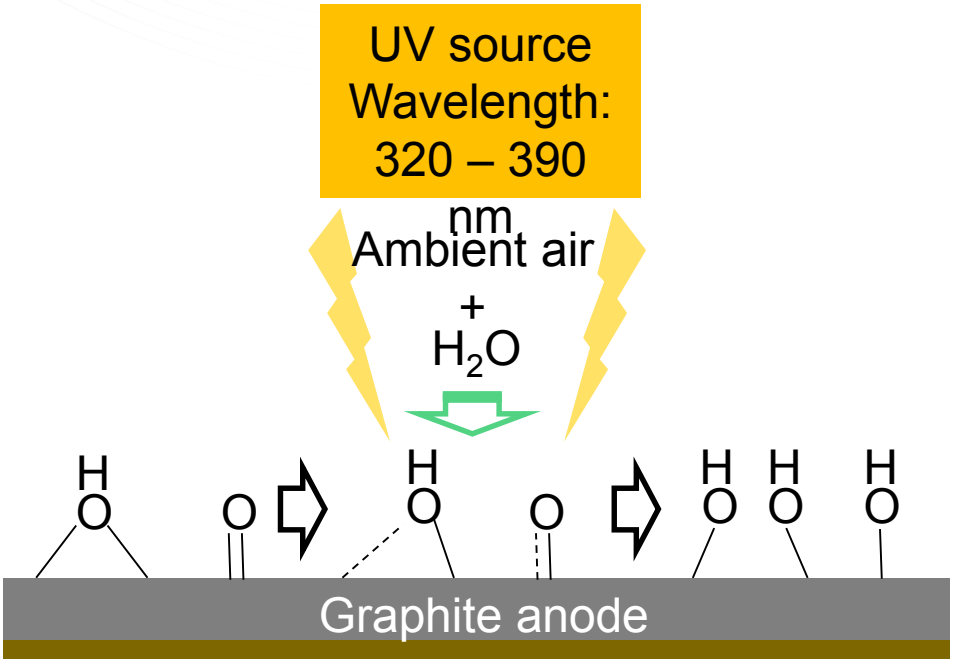
Technical Accomplishments – UV Light Can Control Oxygen Levels on Graphite Surfaces, Helping Initial Formation of Anode SEI Layer

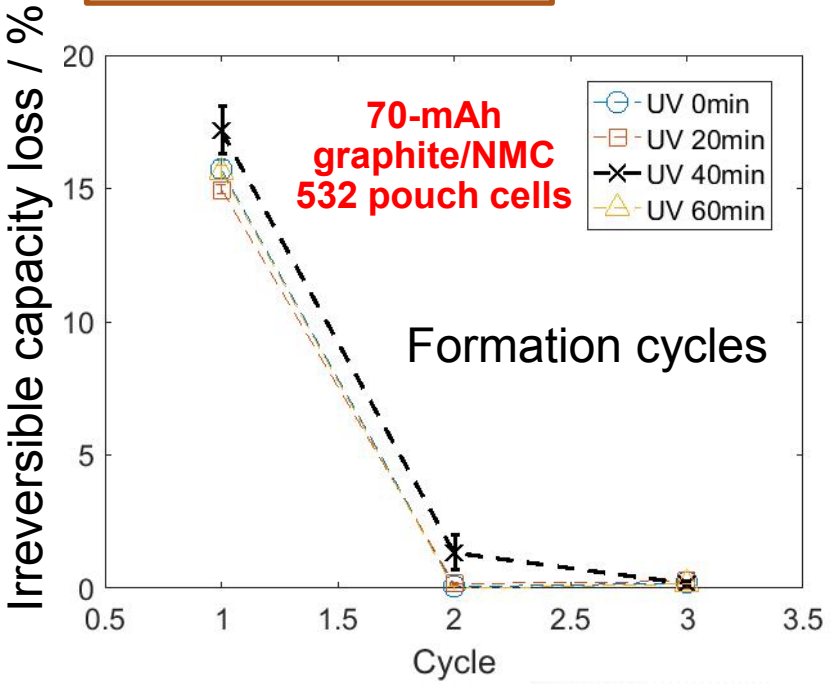
Oxygen levels on graphite surfaces can be controlled using UV light in ambient air

Increasing interactions between lithium ions in electrolyte and electron rich oxygen atoms on graphite

Improving electrolyte wetting to graphite and reduction reaction on graphite surfaces during formation cycles

Stable /robust initial SEI

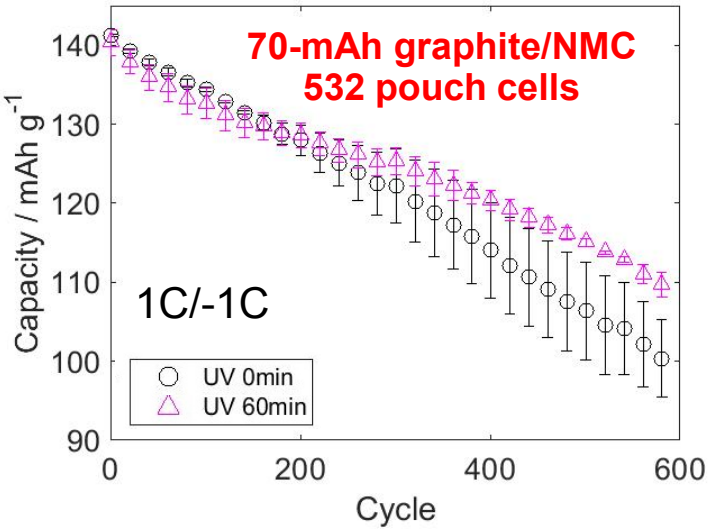




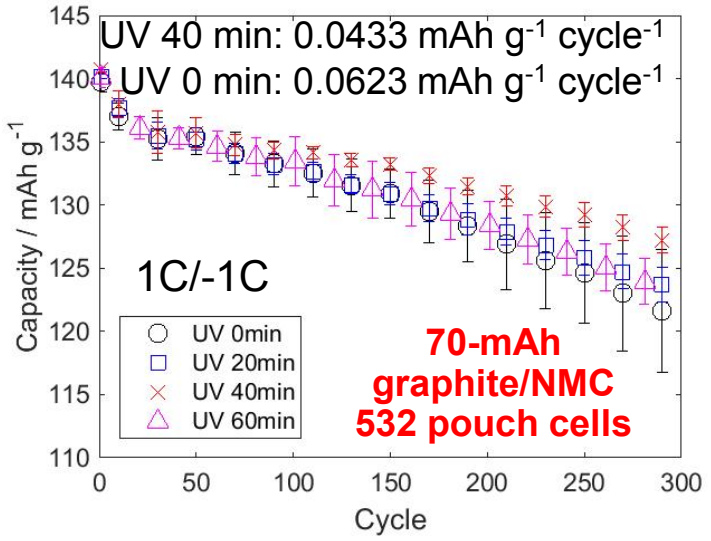
Irreversible capacity loss is higher for graphite anode having UV treatment for 40 minutes during formation cycling, indicating more chemical interactions between graphite and electrolyte.

S.J. An et al., *J. Electrochem. Soc.*, **163**, A2866 (2016).

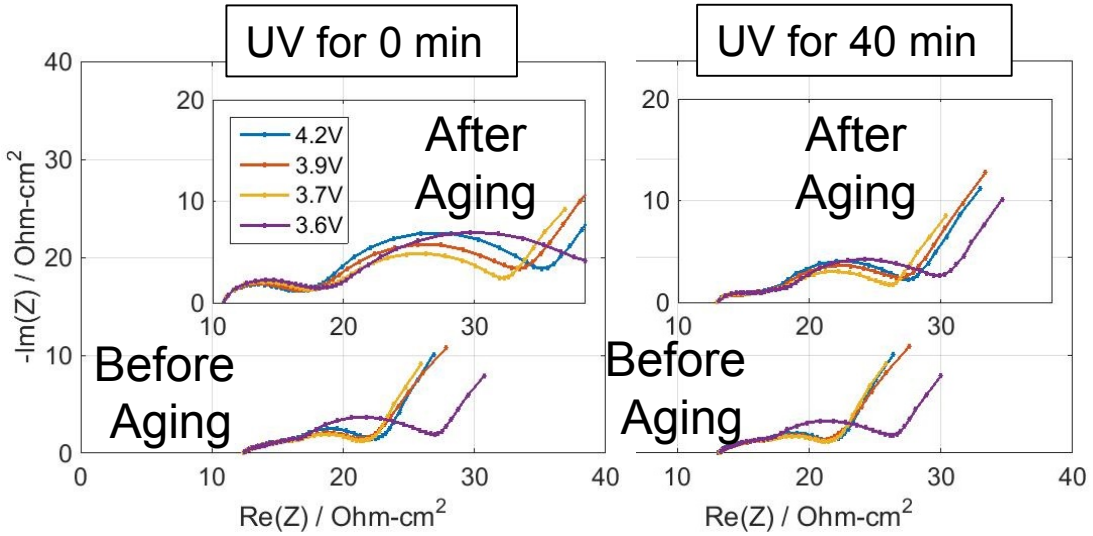
UV Treatment Reduced Charge-Transfer and Surface-Film Resistances and Improved Cycle Life

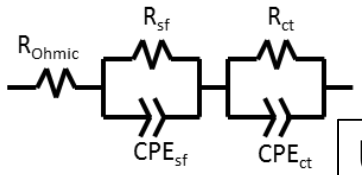


Pouch cell feasibility test (600 cycles): higher capacity retention after UV treatment

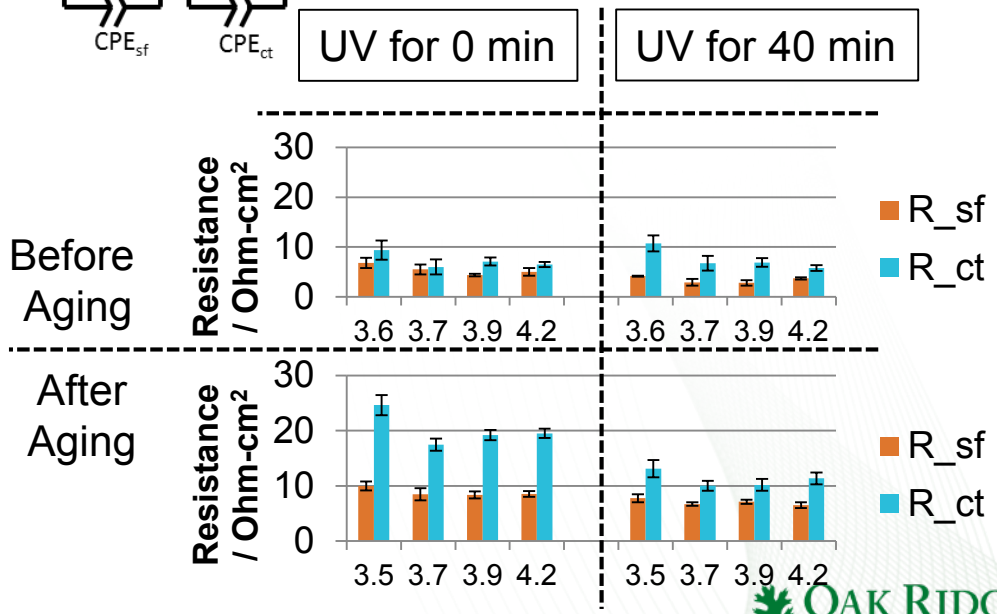


UV optimimzation in pouch cells: highest capacity retention for 40 min of UV





R_sf = surface film (SEI layer) resistance
R_ct = charge transfer resistance



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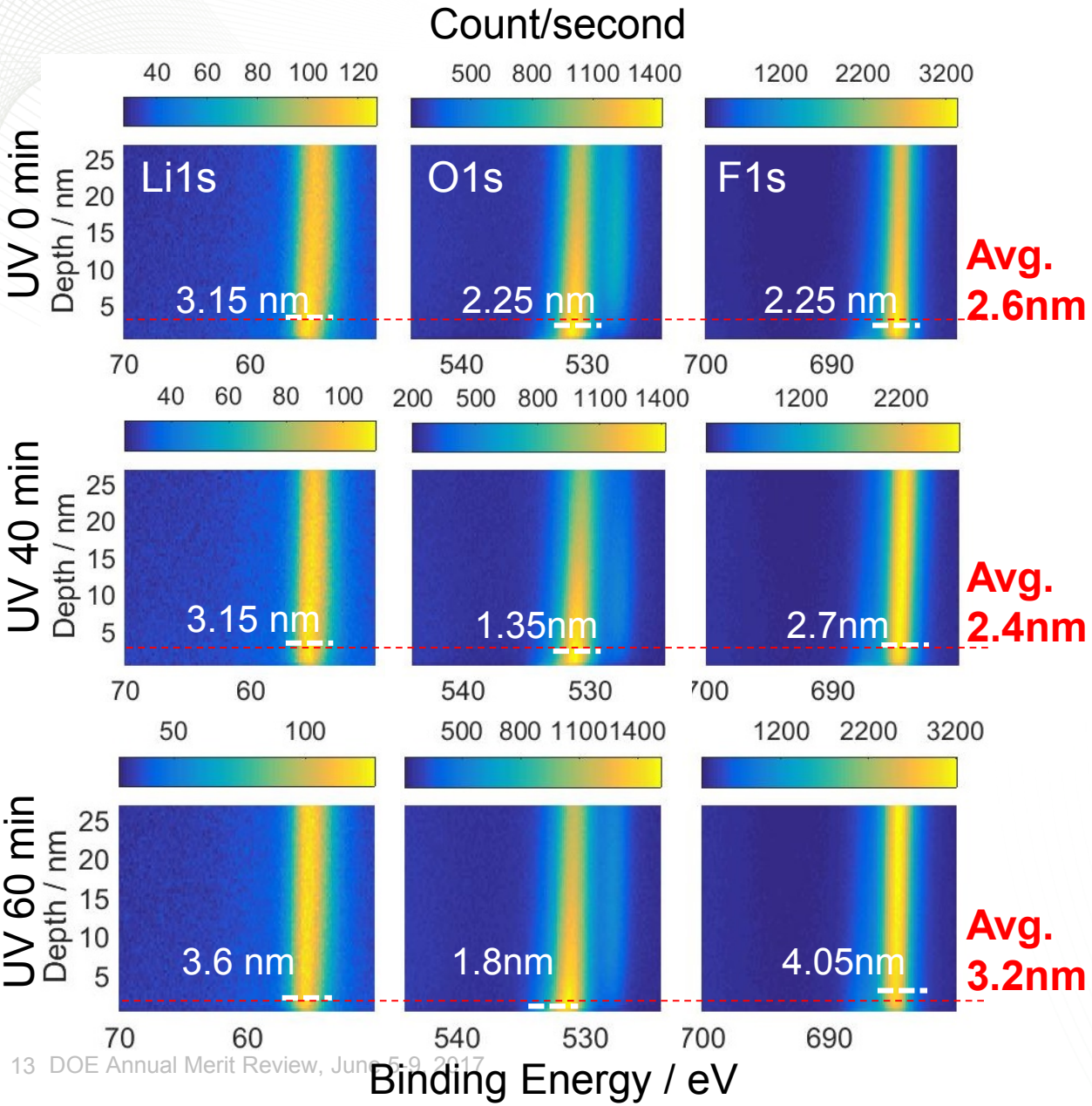
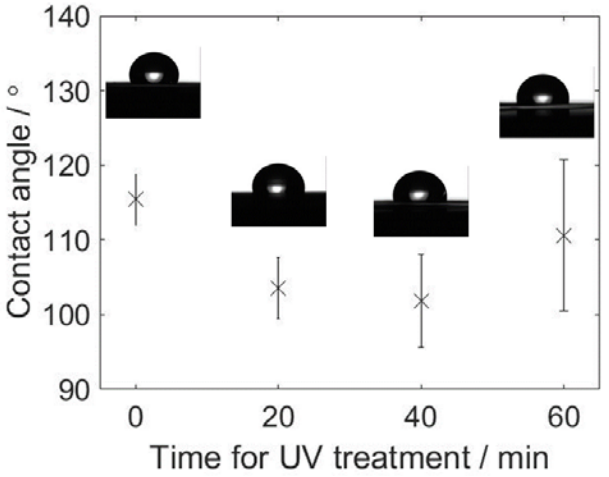
XPS Depth Profiling Revealed Optimum Treatment Time and Was Correlated with Water Contact Angle

S.J. An et al., *J. Electrochem. Soc.*, **163**, A2866 (2016).

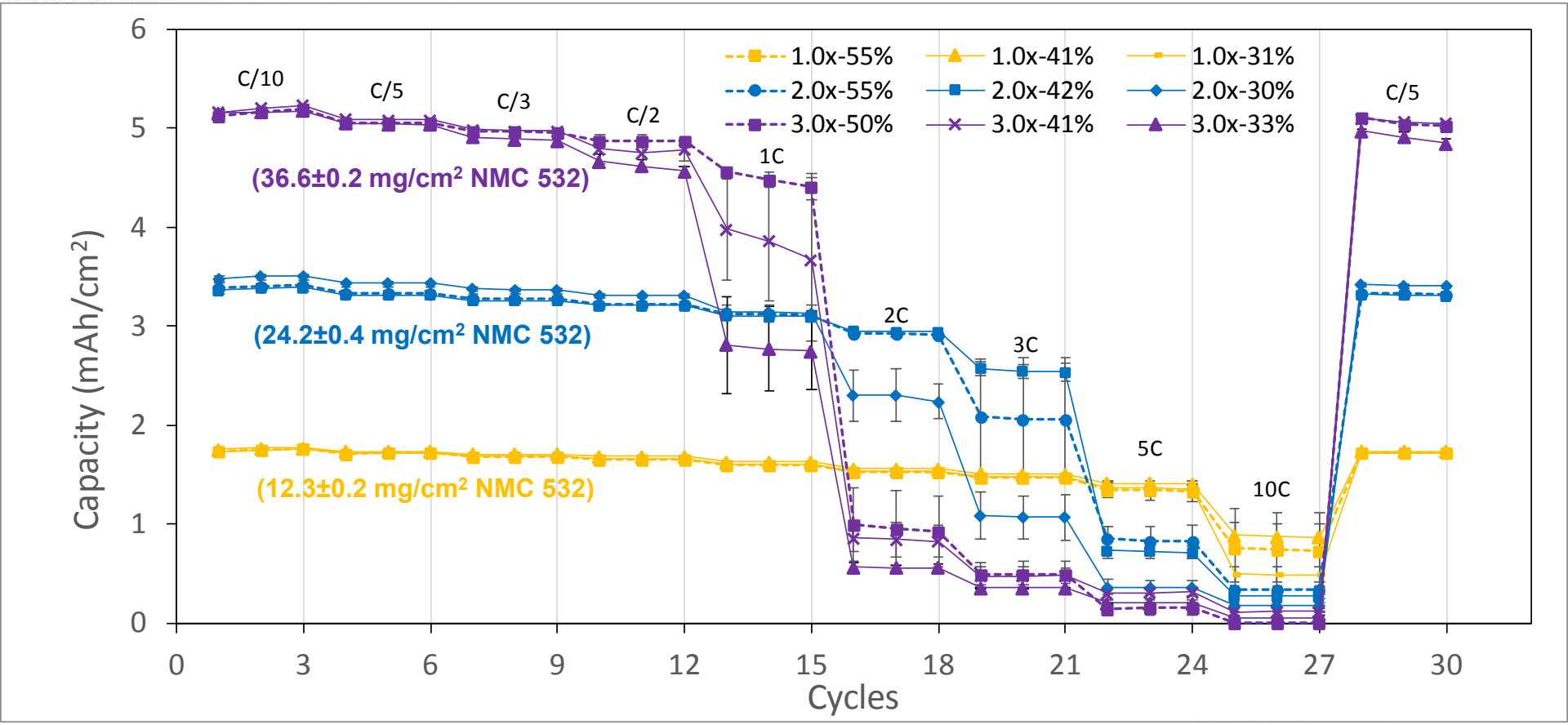




Low contact angle after UV treatment for 40 min.

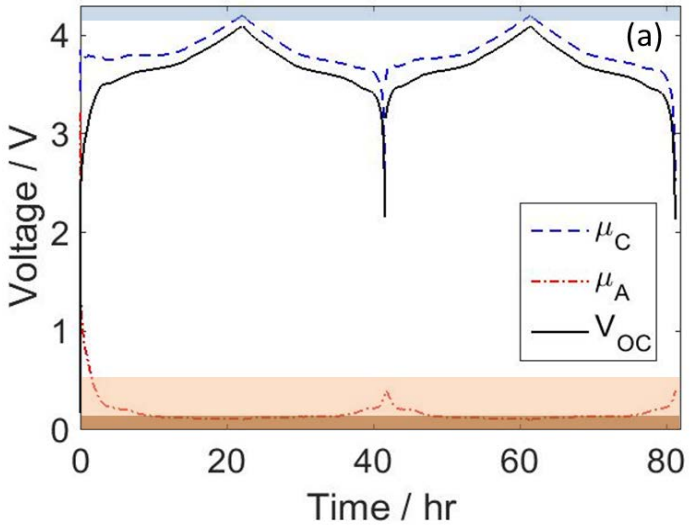
The thickness of surface film (SEI) decreased after 40 min of UV treatment and increased again after 60 min of treatment time, indicating an optimum exposure time exists.

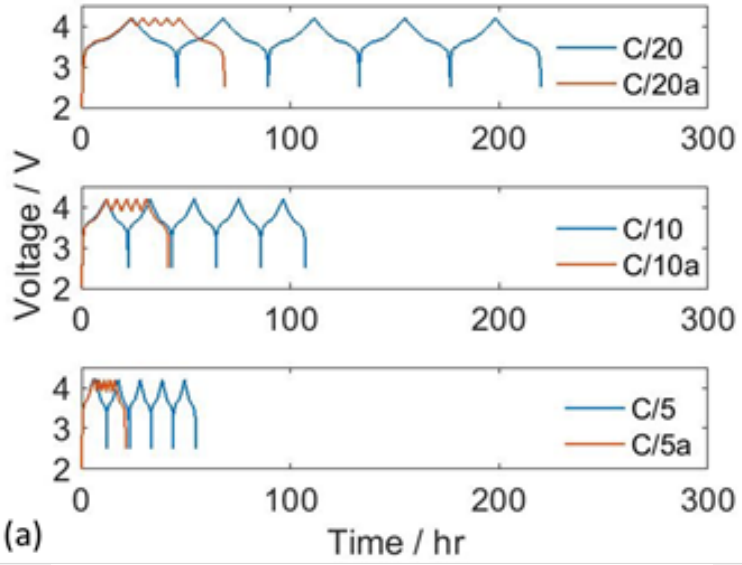
Technical Accomplishments – Half-Cell Cathode Thickness and Porosity Sensitivity Study



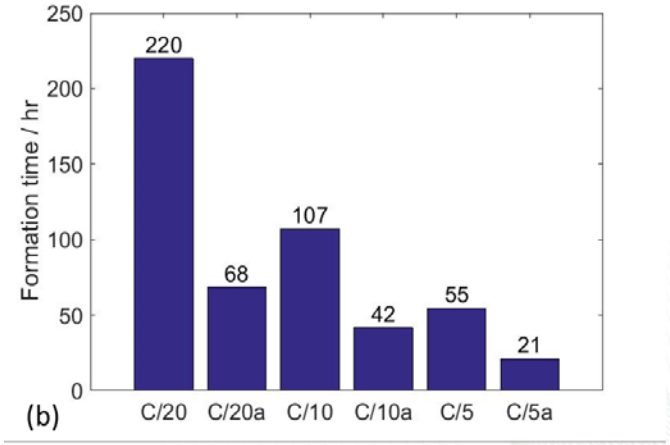
- **For thick electrodes, calendered porosity was found to dramatically affect performance in the 1-5C discharge range.**
- **Higher porosity (50%) was beneficial for 5.2 mAh/cm² loadings.**
- **At 1C, *volumetric capacity* (mAh/cm³) was roughly equivalent for 1.0× (12.3 mg/cm²) loading at ~30% porosity and 3.0× (36.6 mg/cm²) loading at ~50% porosity.**

Technical Accomplishments – Dramatically Reduced Formation Cycle Time



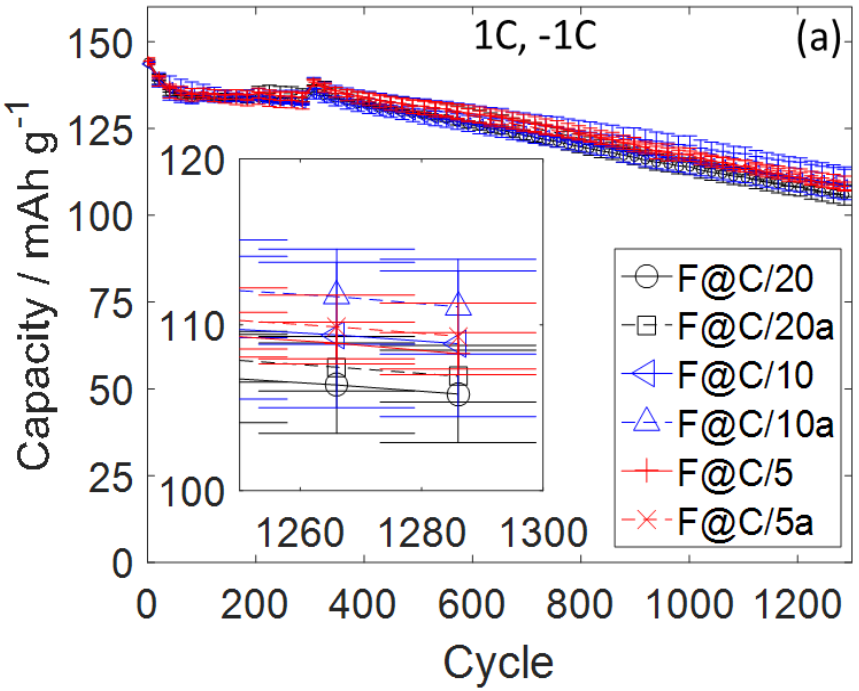


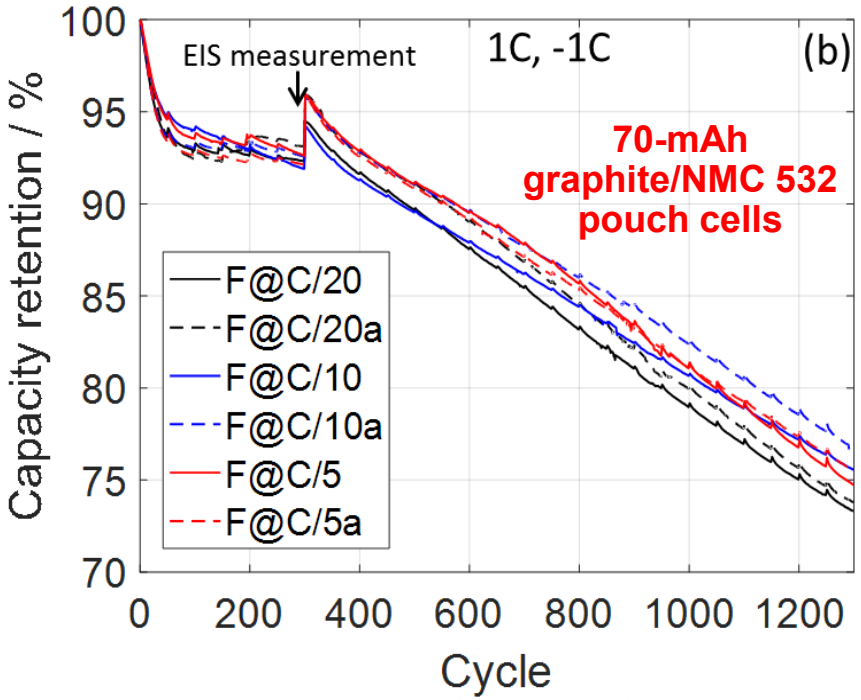
- 5 full charge/discharge cycles were replaced with 1 full charge, repeated shallow cycling at high voltage, and 1 full discharge.
- Shallow cycling at high voltage provides a more robust and chemically stable SEI layer, as evidenced by EIS and long-term cycling data.
- Shortened ORNL formation protocol to <1 day.



S.J. An et al., *J. Power Sources*, **342**, 846 (2017).

Technical Accomplishments – Pouch Cell Cycling Performance with Various Formation Protocols





- **C/10 formation protocols statistically outperformed C/20 protocols (a).**
- **C/5a formation protocol was statistically equivalent to C/20 protocol → ~90% reduction in formation time (a).**
- **C/10a formation protocol outperformed C/20 protocol by ~200 1C/-1C cycles in terms of capacity fade to 80% (b).**

S.J. An et al., *J. Power Sources*, **342**, 846 (2017).

Collaborations

- Partners

- Collaborative Activities
  - **Formation and wetting time reduction and electrode formulation development with XALT Energy.**
  - **Development and implementation of water-based binder suppliers for aqueous electrode formulations.**
  - **Integration of carbon nanotubes with Molecular Rebar Design to reduce conductive additive content.**
  - **Optimization of drying protocols for aqueous and NMP electrode formulations with ANL and B&W MEGTEC.**
  - **Coating deposition physics studies with Texas A&M University.**

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Future Work

- **Remainder of FY17**
  - **Complete electrolyte stability study (Phase 2 and 3) with NMC cathode materials.**
  - **Fully elucidate benefits of improved formation protocol and anode UV treatment using TEM, EELS, and EDS.**
  - **Complete optimization of calendering conditions (thickness vs. porosity tradeoffs) for thick cathode coatings (>5 mAh/cm^2).**
- **Into FY18**
  - **Collaborate with ANL CAMP facility on thick electrode coating and testing standardization.**
  - **Systematic study of Ni-rich cathode compatibility with aqueous processing, including correlation of capacity fade with advanced materials characterization.**
  - **Investigate different Si anode active material manufacturing methods on electrode processing and cell performance.**
  - **Push combined formation/wetting time to <24 h.**

Any future work is subject to change based on funding levels.

Summary

- **Objective:** Generate deep understanding of process-property-performance relationships that lead to lower cost and higher performing lithium-ion cells.
- **Approach:** .
  - Enable thick electrode coatings with next generation cell chemistries (NMC 811, NCA, Si/graphite, etc.).
  - In-depth study of interrelationship of electrode processing steps.
  - Generate processing science knowledge that can be used to strengthen US domestic lithium-ion battery supply chain.
- **Technical:**
  - Determined stability of NMC active materials in water for aqueous cathode processing.
  - Correlated cathode areal loading and porosity with calendering parameters.
  - Developed fast formation cycle and anode graphite UV treatment for improved cycle life.
- **Collaborators:** Broad array of collaborators consisting of battery makers, material suppliers, equipment makers, national labs, and universities.
- **Commercialization:** High likelihood of commercial adoption of processing technologies and licensing due to wide applicability of knowledge generated.

Acknowledgements

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- ORNL Contributors:
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  - Kevin Hays
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Technical Collaborators

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- Alan Goliaszewski
- Feng Gao
- James Banas
- Gregg Lytle
- Lisa Stevenson
- Kevin Dahlberg
- John Camerdese
- Mike Wixom
- Jerzy Gazda

Information Dissemination and Commercialization

Refereed Journal Papers and Presentations

1. S.J. An, J. Li, C. Daniel, H.M. Meyer, III, S.E. Trask, B.J. Polzinn, and D.L. Wood, III, "Electrolyte Volume Effects on Electrochemical Performance and Solid Electrolyte Interphase in Si-Graphite/NMC Lithium-Ion Pouch Cells," *ACS Applied Materials & Interfaces*, Accepted, 2017.

2. Z. Liu, D.L. Wood, III, and P.P. Mukherjee, "Evaporation Induced Nanoparticle – Binder Interaction in Electrode Film Formation," *Physical Chemistry Chemical Physics*, Accepted, 2017.

3. D.L. Wood, Jianlin Li, Zhijia Du, Yangping Sheng, Kevin Hays, Marissa Wood, Lamuel David, Chengyu Mao, Rose Ruther, Seong Jin An, and Nathan Phillip, "Manufacturing R&D for Low-Cost, High-Energy-Density Lithium-Ion Batteries for Transportation Applications," International Battery Seminar, Fort Lauderdale, Florida, March 22-23, 2017. **(Invited)**

4. S.J. An, J. Li, Z. Du, C. Daniel, and D.L. Wood, III, "Fast Formation Cycling for Lithium Ion Batteries," *Journal of Power Sources*, **342**, 846–852 (2017).

5. S.J. An, J. Li, D. Mohanty, C. Daniel, B. Polzin, J. Croy, and D.L. Wood, III, "Correlation of Electrolyte Volume and Electrochemical Performance in Lithium-ion Pouch Cells with Graphite Anodes and NMC532 Cathodes," *Journal of The Electrochemical Society*, Accepted, 2017.

6. S.J. An, J. Li, C. Daniel, and D.L. Wood, III, "Design and Demonstration of Three-Electrode Lithium-Ion Pouch Cells," *Journal of The Electrochemical Society*, Submitted, 2017.

7. S.J. An, J. Li, Y. Sheng, C. Daniel, and D.L. Wood, III, "Long-Term Lithium-Ion Battery Performance Improvement via Ultraviolet Light Treatment of the Graphite Anode," *Journal of the Electrochemical Society*, **163**, A2866–A2875 (2016).

8. S.J. An, S. Nagpure, J. Li., C. Daniel, D. Mohanty, and D.L. Wood, III, "The State of Understanding of the Lithium-Ion-Battery Graphite Solid Electrolyte Interphase (SEI) and Its Relationship to Formation Cycling," *Carbon*, **105**, 52–76, 2016.

Thank you for your attention!

Reviewer Comment Slides (New Task – Not Reviewed in FY16)